

Validation of a gamma-spectrometric method for the measurement of $^{226,228}\text{Ra}$ in environmental media relevant to the offshore oil and gas industry

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The offshore production of oil and gas leads to naturally occurring $^{226,228}\text{Ra}$ being brought to the surface along with produced water. Assessment of potential environmental exposures, if any, requires accurate, precise and practical methods for the measurement of low concentrations of $^{226,228}\text{Ra}$. A method for the simultaneous measurement of $^{226,228}\text{Ra}$ in marine sediments, biota and produced water at a sensitivity of 0.01 pCi/g using high-sensitivity, high-resolution gamma-spectrometry was subjected to an interlaboratory exercise using U.S. commercial laboratories to validate its accuracy, precision, robustness, and sample throughput. The prescribed method involves direct counting for solid samples and a simple $\text{Pb}(^{133}\text{Ba,Ra})\text{SO}_4$ co-precipitation procedure for water samples followed by gamma-counting. Analytical results received from the participating laboratories were subjected to data analysis and statistical evaluation to validate the overall performance of the prescribed method. Relatively good precision and high accuracy of data were achieved when the participating laboratories followed the prescribed procedure closely. The consistency of results among laboratories was not correlated to the $^{226,228}\text{Ra}$ concentrations in the samples. Most of the results that failed the acceptance criteria were either due to the absence of geometric and secular equilibrium between ^{226}Ra and its signature decay daughters, or due to insufficient counting statistics when laboratories are working close to their detection limits. No significant bias or systematic errors were observed, except for produced water samples where results were biased high compared to the known values.

Introduction

The primordial radioisotopes ^{235}U , ^{238}U and ^{232}Th and their decay daughters comprise the naturally occurring radioactive materials (NORM) that may be present in oil and gas bearing formations and are released as by-products of oil and gas productions. The naturally occurring radionuclides are, to some extent, brought to the surface along with the produced gas, produced fluids such as water, crude oil, and condensate, and solid particles that build up into scales on process equipment or are precipitated as sludges.^{1–3} The NORM of primary concern to the oil and gas industry are ^{226}Ra (^{238}U decay) and ^{228}Ra (^{232}Th decay) due to their radiotoxicity, long half-lives (1605 and 5.75 years, respectively) and long biological residence time by way of incorporation into the skeleton. The need for a standardized NORM analytical procedure for the oil and gas industry has been identified by a previous investigation by Dutch authorities, which concluded that results from NORM analysis on pre-treated, homogenized samples from the oil-gas industry by authorized laboratories with expertise and experience in these types of analyses showed large mutual scatter in analytical data.⁴ Accurate, reliable and robust NORM analytical techniques are essential due to the highly specific and complex nature of NORM samples relevant to the oil and gas industry. Produced water can have total dissolved solid content of 5 to 300 g/l of chloride and sulfate salts of Na, K, Mg, Ca and Ba. The alkaline

earth metals have similar chemical behavior as Ra and can pose potential interferences in the chemical analysis.

Reliable, practical and accurate sampling and analysis methods are needed to assess potential environmental exposures. Sampling protocols, which could be expected to effect significant contribution to the uncertainty of the Ra analytical results, are not addressed herein. An intercomparison test program was set up to assess the potential of the gamma-spectrometry based radioanalytical technique being proposed by Lawrence Livermore National Laboratory (LLNL) as a NORM analysis method for environmental samples relevant to the oil and gas industry. Spiked samples of sediments and dried, homogenized fish and produced water were submitted to commercial radioanalytical laboratories in the United States. Five laboratories were selected based on their technical capabilities, personnel qualification and experience, sample handling capacity (throughput), radiometric counting facility competency, competitive pricing, and previous performance in other radiochemical intercomparison studies.

The results of the intercomparison test program are evaluated in the present report, which is Phase IV of the project “NORM Analysis for Oil and Gas Operations” sponsored by the American Petroleum Institute, the Gas Technology Institute and the U.S. Department of Energy. Phase I involved an extensive review of the technical literature covering 1960 through 1996 to evaluate various analytical methods for the quantitative assay of $^{226,228}\text{Ra}$ in environmental media.⁵ The criteria

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for the selection of analytical techniques appropriate for the NORM Project were: high accuracy and good precision, a sensitivity of 0.01 pCi/g or 0.01 pCi/ml for ^{226}Ra or ^{228}Ra , applicability to environmental media of primary interest to offshore oil and gas operations, low analytical cost, a method that could be readily implemented by existing commercial radiochemical laboratories, high sample throughput through use of simple sample chemical processing steps and short, practical nuclear counting periods.

The most promising methods identified in Phase I were then experimentally tested in LLNL laboratories during Phase II of the NORM Project using radiochemically spiked samples of dried fish, sediments and produced water to assess the practical advantages and disadvantages of the different methods.⁶ Low-background, high-resolution gamma-spectrometry employing high purity germanium detectors was the technique of choice due to its capability for simultaneous determination of $^{226,228}\text{Ra}$ with a minimum of chemical separation steps. Sludges, sediments and biota can be assayed by direct counting, while produced water can be subjected to a simple, yield-traceable Pb(Ra)SO_4 coprecipitation procedure for enhanced analytical sensitivity. Since the radiometric counting steps rely on the measurement of gamma-rays from the daughters of ^{226}Ra decay chain, which has the gaseous ^{222}Rn as an intermediate progeny, properly sealed, gas-tight sample packaging for gamma-counting and sufficient decay ingrowth period for the attainment of geometric and secular equilibrium are critical for accurate analysis. Phase III of the NORM project involved developing the sampling and analysis plan for the interlaboratory test program.⁶ The present paper summarizes the evaluation of analytical data from participating laboratories to validate the performance of the proposed LLNL method as well as to identify, if present, sources of any systematic differences between laboratories, general trends and potential problem areas.

Experimental

Sample collection and preparation

Performance evaluation (PE) samples were prepared at LLNL by gravimetric dilutions and quantitative transfers of standard solutions to provide the desired "known" activities of ^{226}Ra and ^{228}Ra . Standard reference materials SRM 4967 (^{226}Ra) and SRM 4339A (^{228}Ra) from the U.S. National Institute of Standards and Technology (NIST) were used as parent stock solutions. For biota samples, the flesh of fresh fish was dried (not ashed) slowly in an oven to prevent spattering and then ground and homogenized with a ball mill. About 25-gram aliquots were sub-sampled from the stock material for distribution to the analytical

laboratories. Each aliquot was wetted with 2N nitric acid to a final volume of about 100 ml and allowed to sit for at least 24 hours prior to addition of known volumes of the $^{226,228}\text{Ra}$ spike standard solutions for equilibration of spike activity. By adding enough water to fill all interstitial voids in the solid matrix, the spike radionuclide is distributed evenly throughout the entire mass without significant precipitation or ion exchange that could lead to inhomogeneity in the activity distribution. Aliquot sizes of about 25 grams (dry weight) per sample were distributed to the participating laboratories in this "wetted" condition to prevent fractionation or localization of the radioactivity spike during sample transit and prolonged standing. The laboratories were instructed to dry the entire sample in an oven at 300 °C for at least 4 hours and homogenize it prior to sample analysis. Quadruplicate baseline high-sensitivity gamma spectrometry at LLNL for $^{226,228}\text{Ra}$ concentrations in the fish stock material showed none detectable levels at 0.01 pCi/g.

Pseudo-sediment PE samples were prepared by mixing LLNL-site soils, "blank" sand, and adding the appropriate amounts of $^{226,228}\text{Ra}$ standard solutions to give the desired activity concentrations. Baseline activity levels for Ra for the LLNL soils were determined to be 0.511 ± 0.012 pCi/g ^{226}Ra and 0.615 ± 0.022 pCi/g ^{228}Ra by high-sensitivity gamma-spectrometry on four replicate analyses, each counted for 5 days. Mallinco-dkt™ 7062 acid-washed and dried sand served as "blank" sand. Four replicate analyses on the sand sample by high-sensitivity gamma-spectrometry indicated baseline activity levels of 0.714 ± 0.005 pCi/g ^{226}Ra and 0.030 ± 0.006 pCi/g ^{228}Ra . The mixture of soil and sand is homogenized and wetted with 150 ml of 2N nitric acid and allowed to sit for at least 24 hours prior to addition of known amounts of the $^{226,228}\text{Ra}$ spike standard solutions. Aliquot sizes of about 300 grams (dry weight) per sample were distributed to the participating laboratories in this "wetted" condition to prevent fractionation or localization of the radioactivity spike during sample transit and prolonged standing. The laboratories were instructed to dry the entire sample in an oven at 300 °C for at least 4 hours and homogenize it prior to sample analysis.

Produced water samples (PW) were collected by Core Laboratories (Houston, TX) from an oil operation platform in the Gulf of Mexico. The samples were pre-treated and characterized at LLNL prior to distribution to the participating laboratories. Six replicate analyses on the untreated sample by high-sensitivity gamma-spectrometry, each counted for 5 days, gave baseline activity levels of 0.47 ± 0.01 pCi/ml ^{226}Ra and 0.34 ± 0.01 pCi/ml ^{228}Ra . At these high baseline levels, it was not necessary to add known amounts of the Ra standard solutions. Hence, PE samples were prepared by

quantitative dilutions using double distilled, de-ionized water acidified to pH 2 with concentrated nitric acid to arrive at the desired concentration levels. Due to the high total dissolved solid (TDS) content of the PW samples, continuous stirring was employed during the sub-sampling operation. Aliquot sizes of 500 ml of the diluted PW samples were distributed to the analytical laboratories.

Table 1 summarizes the sample composition and activities. The gravimetric concentration (i.e., the quotient of the activity added to the mass of the matrix) of ^{226}Ra and ^{228}Ra in the prepared samples were considered as the reference (“known”) activities of the PE samples. The PE samples, after their preparation, were not characterized at LLNL with actual laboratory analysis for validation of their “true” values. The known gravimetric concentration should be a fairly accurate representation of the true activity when contamination is not present, baseline in the host matrix is negligible or can be corrected for, and the activity added is homogeneously distributed throughout the matrix. Failure of these assumptions will express themselves as systematic errors or a one-sided bias in the analytical results reported by the laboratories. Moreover, if replicate analyses must be made, the recommended procedure is to use different sample sizes to detect errors that are functions of the sample size. This latter principle was not adopted in the present round-robin exercise.

Radioanalytical methods

The general steps of the analytical procedures are presented in Fig. 1. Briefly, sediment or biota samples are dried in an oven and homogenized. The dried sample

Table 1. Sample matrices, size and activity concentrations of $^{226,228}\text{Ra}$ employed in the interlaboratory round-robin exercise

Sample matrix	Sample size	Nominal activity	
		^{226}Ra	^{228}Ra
Biota	25 g	0.1 pCi/g	0.1 pCi/g
		0.5 pCi/g	0.5 pCi/g
		1.0 pCi/g	1.0 pCi/g
Sediment	300 g	0.2 pCi/g	0.2 pCi/g
		0.5 pCi/g	0.6 pCi/g
		1.0 pCi/g	1.0 pCi/g
Produced water	500 ml	0.02 pCi/ml	0.017 pCi/ml
		0.05 pCi/ml	0.033 pCi/ml
		0.24 pCi/ml	0.168 pCi/ml

Triplicate samples per matrix per activity concentration were sent to participating laboratories. A matrix blank is added to each set of three samples. For calculation of final results, participating laboratories were instructed to use a base weight of 300 g for the biota and sediment samples and a base volume of 1 liter for the produced water samples. Reference date for decay correction is 02-January-1998, 1200 PST.

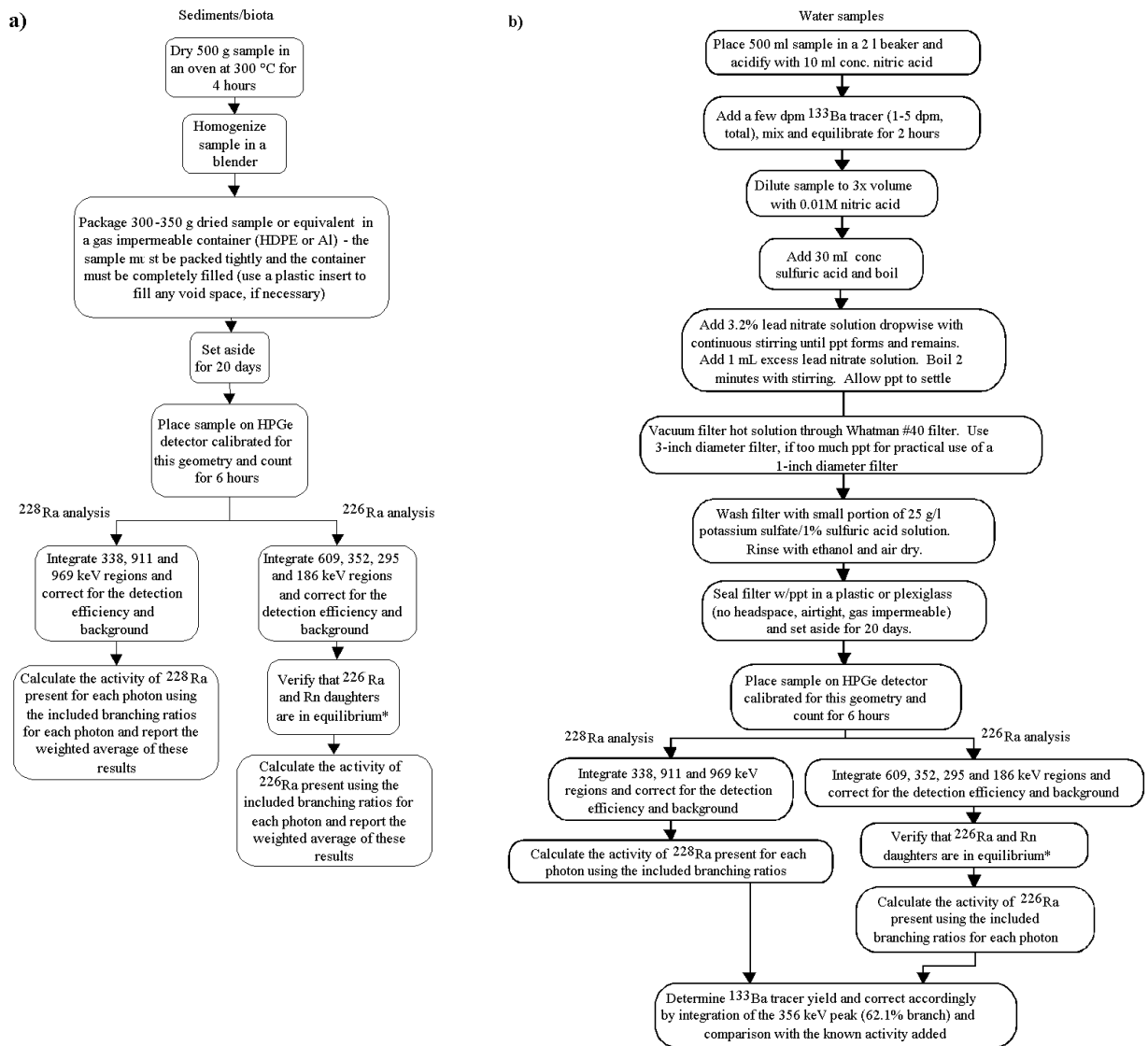
is packed firmly to fill entirely a gas impermeable container making sure no headspace is created and the lid sealed air tight to ensure that the radon gas daughter is not lost to emanation. Loss of radon gas will lead to highly inaccurate results. The packaged sample is set aside for at least 20 days to allow secular equilibrium between ^{226}Ra and its daughters to be attained. The sample is gamma-counted with a low-background high-purity germanium spectrometer calibrated against the same counting geometry as the sample. The activity of ^{226}Ra is quantified using peak analysis of the gamma-rays of its daughters ^{214}Bi and ^{214}Pb , while ^{228}Ra is assayed from the peak analysis of the gamma-rays of its daughter ^{228}Ac . For the PW sample, Ra is extracted by co-precipitation with PbSO_4 . The recovery of the chemical procedure is assessed using a known tracer amount of the gamma-emitting nuclide ^{133}Ba . The $\text{Pb}(\text{Ba},\text{Ra})\text{SO}_4$ precipitate is dried and packaged following similar precautions adapted with the biota/sediment samples. An ingrowth period of at least 20 days is allowed for secular equilibrium. The activities of $^{226,228}\text{Ra}$ are quantified by gamma-spectrometry following the protocol used with the biota/sediment samples.

Special requirements

So that results could be obtained and interpreted at the same precision, prescribed sample size, analytical procedures, counting time and efficiencies, chemical yielding, nuclear data, gamma-calibration standards and procedures were stipulated at the onset of the program. The gamma-spectrometric nuclear data to be used in the analysis were provided to the laboratories and are presented in Table 2. Standard reporting formats were issued with each sample. In addition to the measured activity levels of $^{226,228}\text{Ra}$, participants were encouraged to include as much relevant and sufficient information as they can to allow critical review of the analytical results or recalculation of data by the LLNL NORM group. This shall include 1σ associated uncertainty, chemical yield, counting period, sample and background count rates in each energy region of interest encompassing the radionuclides given in Table 2, and the calculated minimum detectable activity. Participants were also encouraged to include comprehensive case narratives of experiences met with the analytical process and to submit the relevant laboratory logbook as supplements to the case narratives.

Data analysis and statistical evaluation

A large amount of data was accumulated in this interlaboratory exercise and it would be impossible to tabulate all these data or to examine them in detail here.

Fig. 1. Analytical steps in the determination of $^{226,228}\text{Ra}$ in biota or sediment (a), and produced water samples (b)Table 2. Prescribed nuclear data for the gamma spectrometric analysis of $^{226,228}\text{Ra}$ ⁷

Nuclide	Gamma-energy, keV	Branching ratio	Comments
^{228}Ra (^{228}Ac)	338.7	0.119	
^{228}Ra (^{228}Ac)	911.2	0.272	
^{228}Ra (^{228}Ac)	968.8	0.164	
^{226}Ra	186.14	0.035	Used to check for secular equilibrium with daughters
^{226}Ra (^{214}Bi)	609.27	0.448	
^{226}Ra (^{214}Pb)	351.92	0.358	
^{226}Ra (^{214}Pb)	295.2	0.1839	
^{133}Ba	355.86	0.621	Used as chemical yield tracer for the PW samples
^{235}U	185.7	0.54	Used to correct for interference in the 186-keV gamma-peak
^{235}U	143.8	0.106	

The comprehensive data that were compiled and the details of the statistical analyses are reported elsewhere.⁶ Data were evaluated using relatively simple statistical analysis of the mean, the standard error, the range analysis, the normalized deviation from the known value and control chart analysis for the laboratory mean, standard deviation and range was used to test the goodness of precision. Generalizations obtained from the evaluations of the analytical data are discussed in the present paper.

Results and discussions

Measurement errors or uncertainties

All participating laboratories reported only the gamma-counting errors as the $\pm 1\sigma$ errors associated with the measurement as opposed to the ideal overall measurement uncertainty. This shortcoming can be attributed to the lack of guidance on this parameter since it was not explicitly stipulated in the statement of work supplied to the laboratories. Moreover, if guidance is to be recommended, the exact algorithm for propagating errors should be specified so it can be standardized among the laboratories for purposes of comparisons. Most laboratories resort to the deeply ingrained habit of quoting only the $\pm 1\sigma$ counting error as the uncertainty in the measurement and assuming that all other sources of uncertainty are insignificant. This is a reasonable assumption only if the activities being measured are very close to background. Otherwise the other sources need close consideration. Uncertainties arising from the counts detected will clearly vary with the activity measured and the count time employed in the analysis.

Minimum detectable concentration (MDC)

A minimum counting time of 1000 minutes is required to attain the 0.01 pCi/g (ml) detection limit given the sample sizes used in this exercise and the typical detector background and counting efficiencies in participating commercial laboratories. Two laboratories indicated that any counting period longer than 1000 minutes will substantially affect their operational sample throughput. In general, the MDCs for ^{226}Ra will be lower than ^{228}Ra for the same sample, counting time and detector. This is due to the higher gamma-emission rates for the daughter gamma-peaks used to quantify ^{226}Ra and the higher gamma counting efficiencies. Sediments will have higher MDCs for the same count time and sample size as the biota and PW samples due to increased matrix attenuation of the gammas.

All participants attained the 0.01 pCi/g (ml) MDC for PW with shorter counting periods. Since chemical separation is employed in the analysis, larger sample sizes can be processed and with Ra preconcentrated by

co-precipitation, when collected on a membrane filter for gamma counting, much higher geometrical counting efficiency can be realized. A critical factor that influences the sensitivity of the analysis for PW is the chemical recovery quantified with the use of a ^{133}Ba tracer. Overall, the recovery is better than 70% and as high as 90%. The reproducibility shows a wide range, however, with a 3–30% standard deviations.

Nuclear data and calibration standards

It is vital to use the correct calibration standards in order to obtain meaningful results. Moreover, a standard that is suitable for one matrix may be inappropriate for other matrices. Presently there is a lack of suitable calibration sources in solid matrices such as the sediment and the biota samples. It would also be useful in the case of PW, which has physico-chemical properties distinct from most environmental waters, to have an appropriate calibration standard. Due to such limitations, participating laboratories were encouraged to prepare sources for gamma-detector calibration using NIST traceable $^{226, 228}\text{Ra}$ standards in base matrices employing fish, soil or sediments, and high total dissolved aqueous matrices. Three laboratories prepared calibration standards using $^{226, 228}\text{Ra}$ sources as recommended by LLNL, while the rest used a mixed radionuclide standard consisting of a mixture of radionuclides ($^{226, 228}\text{Ra}$ was not part of the suite of nuclides) that emit a single gamma-ray to enable straightforward calibration of a gamma-detector. Review of their calibration data indicated a bias of 3–5% on the high side for the signature gamma-peaks of $^{226, 228}\text{Ra}$, which would lead to lower radium activities when compared with the known values. Most laboratories prepared calibration standards using soil and dried fish as base matrices. One laboratory used non-iodized table salt as the base material in its calibration. This is expected to lead to a bias of 2–3% lower than the known values due to the distinct composition and density of salt from that of soils or sediments.

Derived ratios of measured-to-known values

Based on the observed ratios, there appears to be no correlation between consistencies in the measured results between laboratories and the concentration levels of either ^{226}Ra and ^{228}Ra in any of the matrices under study. This is a good indication of the applicability of the proposed analytical techniques for these matrices over a wide range of concentration levels covering 2 to 100 times the desired detection sensitivity of 0.01 pCi/g (ml). Replicate analyses gave results that were highly precise, but the accuracy was not as good as the precision. Laboratories which followed the prescribed analytical and gamma-calibration procedures as closely

as possible as their resources would allow and employed the LLNL-recommended nuclear data obtained high precision and accuracy. The rather high internal precisions in the measurements imply that sample homogeneity has been achieved in the preparation of the “spiked” PE samples. Thus it can be concluded that the manner of preparing a “wetted” PE standard in the present study provides for a homogeneous distribution of radioisotope tracers in solid matrices. Among the matrices investigated, the best internal precision and high accuracy results for $^{226,228}\text{Ra}$ were obtained with the sediment samples followed by biota samples. This is probably due in part to the ready availability of calibration standards using soil/sediment or fish as base materials in preparing the sources. In addition, these samples require minimum sample preparation, and such simplicity in procedure eliminates potential sources of error that may be encountered with a chemical separation process, as in the case of PW. The lower precision and accuracy reported with the PW samples may be due in part to the unavailability of a PW base material that laboratories may practice on in preparing calibration standards. The use of the proper activity level of ^{133}Ba tracer (5–10 dpm total) in yielding the separation steps significantly influences the accuracy of the measurement.

Disequilibrium and ^{226}Ra analysis

Better precision and higher accuracy were obtained with the ^{228}Ra measurements compared with those of ^{226}Ra . This is due to the fact that ^{228}Ra is quantified via its immediate, short-lived ($T_{1/2}=6\text{ h}$) daughter ^{228}Ac and thus circumvents the problem of loss of radon gas due to emanation or geometric disequilibrium encountered with the analysis of ^{226}Ra . The recommended analysis for ^{226}Ra by gamma-spectrometry utilizes the gamma-ray peaks of the daughter radionuclides ^{214}Bi and ^{214}Pb to quantify the Ra activity. The decay chain involves the intermediate daughter ^{222}Rn gas. Radon emanates naturally from solid matrices via recoil and diffusion.⁸ Rn is released from the point of production by recoil from the alpha decay of ^{226}Ra , and, being a gas, can migrate through cracks and void spaces in a solid matrix and eventually accumulate in any headspace available above the bulk matrix. The ^{214}Bi and ^{214}Pb daughters will then be distributed inhomogeneously in the sample leading to the phenomenon of geometric disequilibrium. Furthermore, if the sample container is permeable to radon gas, the gas will be lost from the bulk of the sample and secular equilibrium with the ^{214}Bi and ^{214}Pb daughters will not be attained resulting to inaccurate results. Thus the preferred sample container for ^{226}Ra analysis by gamma-spectrometry calls for air-tight

sealed aluminum cans, glass bottles, or high density plastic bottles.

To assess the contribution of geometric and secular disequilibrium in the analysis of ^{226}Ra in the present study, the participating laboratories were required to report the count rates and gamma-peak efficiencies obtained for the ^{226}Ra 186-keV gamma-peak and the signature gamma-peaks (Table 2) of its daughters ^{214}Bi and ^{214}Pb . Ideally, if geometric and secular equilibrium are achieved, the ratio of the 186-keV peak activity to the weighted activities of the peaks from ^{214}Bi and ^{214}Pb should be one. Laboratories that counted samples for at least 1000 minutes to accumulate good counting statistics obtained ratios close to 1. The 186-keV ^{226}Ra gamma-peak sits on a high Compton background and is present in typical gamma-spectrum as natural background interference. The same can be said of the ^{235}U 143-, 163- and 205-keV gamma-peaks if it is desired to extract its contribution to the 186-keV gamma-peak. Most commercial laboratories are not willing to count samples longer than a day due to sample throughput and operational concerns. In the case of sediments, the positive bias in the observed ratios can be attributed to improper correction for ^{235}U .

Conclusions

The high-sensitivity, high-resolution gamma-spectrometry based methodology prescribed by LLNL for the analysis of $^{226,228}\text{Ra}$ in fish, sediments and produced water was proven to be reliable, reproducible and accurate when followed closely. Better than 75% of the samples analyzed came back within $\pm 2\sigma$ of the known values. Obtaining good counting statistics is critical to the success of the method. Careful planning on the sample size to process and the counting time to use is needed to produce statistically valid results at low concentrations of $^{226,228}\text{Ra}$. The analytical technique should have general applicability to other samples highly specific to the oil and gas industry and thus provide for a sound basis for a procedure for $^{226,228}\text{Ra}$ measurement. The method is capable of achieving analytical sensitivities down to 0.01 pCi/g (ml) and is useable in commercial laboratories and within their capabilities. The adoption of a uniform nuclear decay and gamma-yield data and calibration of detector efficiency employing traceable $^{226,228}\text{Ra}$ standards reduce the spread in results to less than $\pm 10\%$. However, a protocol on the reporting of measurement uncertainties (e.g., counting errors versus overall, propagated uncertainties) should be established to further reduce the ambiguities in the analytical results. At the sample sizes employed in this study (i.e., 25 g of biota, 300 g of sediment and 500 ml of produced water), a minimum gamma-counting time of 1000 minutes using standard

high purity germanium (HPGe) gamma-spectrometers of reasonably low background is needed to achieve detection limits of 0.01 pCi/g (ml). The elimination of headspace and ensuring air-tight sealing in the packaging stage of the processed samples for gamma-counting are very critical to obtaining accurate and precise results for ^{226}Ra .

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